

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(13) International Publication Date
22 November 2001 (22.11.2001)

PCT

(10) International Publication Number
WO 01/88075 A1

(51) International Patent Classification⁷: C11D 3/22, 3/37

(72) Inventors: KUMAR, Velayudhan, Nair, Gopa; Hindustan Lever Research Centre, Chakala, Andheri (East), 400 099 Mumbai (IN). MOULEE, Anuradha; Hindustan Lever Research Centre, Chakala, Andheri (East), 400 099 Mumbai (IN).

(21) International Application Number: PCT/EP01/04942

(74) Agents: FRANSELLA, Mary, Evelyn et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(22) International Filing Date: 1 May 2001 (01.05.2001)

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(25) Filing Language: English

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(26) Publication Language: English

Published:

(30) Priority Data:
42/381 31.00 9 May 2000 (09.05.2000) IN
0018287.3 25 July 2000 (25.07.2000) GB

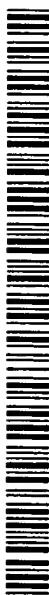
- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(71) Applicant (for PCT only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(71) Applicant (for PCT only): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL, Rotterdam (NL).

(71) Applicant (for PCT only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).



WO 01/88075 A1

(54) Title: SOIL RELEASE POLYMERS AND LAUNDRY DETERGENT COMPOSITIONS CONTAINING THEM

(57) Abstract: Anionic, hydrophobic polysaccharides useful as soil release agents in detergent compositions are graft copolymers of a polysaccharide having anionic substituents with an ethylenically unsaturated monomer, the copolymer having a polysaccharide backbone carrying grafted hydrophobic vinyl polymeric groups derived from the ethylenically unsaturated monomer, and anionic substituents. The polymers exhibit enhanced release of both oily and particulate soil from both polyester and cotton.

- 1 -

SOIL RELEASE POLYMERS AND LAUNDRY DETERGENT
COMPOSITIONS CONTAINING THEM

TECHNICAL FIELD

5

The present invention relates to novel soil release polymers for detergent formulations capable of enhancing soil removal from cotton or polyester fabric or their blends and a process for the preparation of the same.

10

BACKGROUND OF THE INVENTION

The washing of soiled fabrics with a laundry detergent is essentially a two step process. In the first stage, the 15 detergent must remove the soil particles from the fabric and suspend them in the soil solution. In the second stage the detergent must prevent soil particles and other insolubles from re-depositing on the cloth before and after the fabric is removed from the soil solution or the rinse solution.

20 Polymers are known to aid both processes - soil release polymers enhance soil removal from the fabric whilst anti-redeposition polymers prevent the deterged soil from depositing on the fabric.

25 The thrust in recent times has been the development of soil release polymers (SRPs), which can be incorporated into detergent formulations, to enhance the removal of soil from the fabric. SRPs adsorb on the fabric surface, modifying properties like the hydrophilic or hydrophobic nature of the 30 fabric and its surface energy. Consequent soil removal is

- 2 -

greater than what is possible with a conventional detergent formulation.

Soil release polymers disclosed in the literature address the 5 problem of removal of oily or fatty soils from polyester.

Polyester is a hydrophobic fabric and removal of hydrophobic, oily soils from the fabric has historically been a problem.

The problem has been circumvented in part by using soil 10 release polymers which combine hydrophobic and hydrophilic segments. The polymers adsorb strongly on the fabric, are easily dispersed or dissolved in a surfactant and are compatible with the components of the detergent formulation. When incorporated in a detergent formulation, they aid oily soil removal.

15

Various soil release polymers have been disclosed in the prior art for removal of oily soils from polyester. A vast majority are polyesters that have been hydrophilically modified. US3959230 and US4116885 disclose modified 20 polyesters as soil release agents for detergent formulations.

GB2322137 discloses the hydrophobic modification of starch (starch is the hydrophilic segment) and its use as a soil release polymer, in particular for detergency of oily soil 25 from polyester fabric. Hydrophobic modification was carried out by graft copolymerising starch with hydrophobic monomers.

US5227446 discloses a polysaccharide modified with a) a monoethylenically unsaturated dicarboxylic acid/anhydride/alkali metal salt, b) monoethylenically 30 unsaturated carboxylic acid/alkali metal salt and c) monomer

- 3 -

containing two or more ethylenically unsaturated, non-conjugated double bonds in the molecule.

SRPs for removal of oily soil from cotton have also been
5 disclosed. US3948838 discloses the use of copolymers of hydrophobic acrylic monomers and water soluble monomers like acrylic acid, as oily soil release agents for cotton fabrics.

10 Hence, polymers are known in the prior art for removal of oily soil from cotton or polyester. However, polymers that can aid removal of oily and particulate soil or their mixtures from cotton and polyester have not been disclosed.

15 SUMMARY OF THE INVENTION

Thus according to the present invention, novel soil release polymers that are anionic, hydrophobic graft copolymers of polysaccharides are provided. The soil release polymers can
20 be incorporated in detergent formulations and aid the removal of oily and particulate soil from cotton, polyester or their blends. The polymers can also be used in rinse conditioners. A process for making these soil release polymers comprising the steps of anionic modification and
25 graft copolymerisation is also provided.

DEFINITION OF THE INVENTION

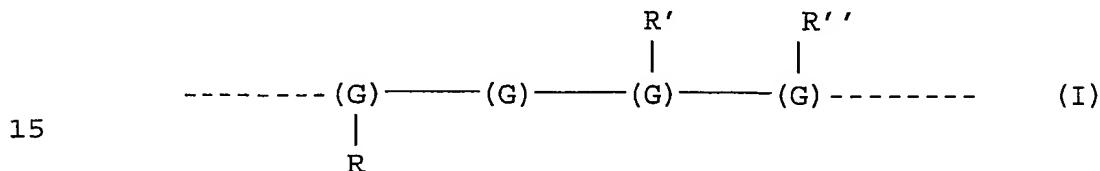
According to a first aspect of the present invention, there
30 is provided an anionic, hydrophobic polysaccharide which is a graft copolymer of a polysaccharide having anionic

- 4 -

substituents with an ethylenically unsaturated monomer, the copolymer having a polysaccharide backbone carrying grafted hydrophobic vinyl polymeric groups derived from the ethylenically unsaturated monomer, and anionic substituents,
5 preferably a group which possesses a carboxylic or a sulphonic acid head group or a salt thereof.

More specifically the invention provides an anionic, hydrophobic polysaccharide having the general formula I:

10



20 wherein R is a hydrophobic vinyl polymer, R' and R'' which may or may not be the same represents a group which possesses a carboxylic or a sulphonic acid head group or a salt thereof and G is a monosaccharide or substituted monosaccharide.

25 According to a second aspect of the present invention there is provided a process for the preparation of an anionic, hydrophobic polysaccharide as previously defined, comprising the steps of graft copolymerisation and anionic modification of a polysaccharide.

30

According to a third aspect of the present invention there is provided a fabric treatment composition comprising a fabric treatment agent and from 0.01 to 10 wt% of a anionic, hydrophobic polysaccharide as previously defined.

- 5 -

According to a fourth aspect of the present invention there is provided a detergent composition comprising from 5 to 60 wt% of a detergentsurfactant and from 0.01 to 10 wt% of an anionic, hydrophobic polysaccharide as previously defined.

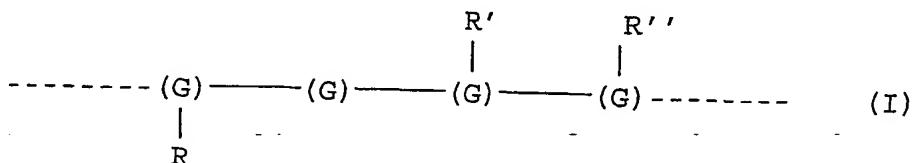
DETAILED DESCRIPTION OF THE INVENTION

The anionic, hydrophobic polysaccharide

10

The anionic, hydrophobic graft copolymer of polysaccharide of the current invention has the general structure given below:

15



20

wherein R is a hydrophobic vinyl polymer, R' and R'' which may or may not be the same, represent a group which possesses a carboxylic or a sulphonate acid head group or a 25 salt thereof and G is a monosaccharide or substituted monosaccharide.

It is preferable that G is a monosaccharide.

30 In a first preferred embodiment, R' and R'' are polymeric vinyl sulphonate groups such as $-(\text{CH}_2-\text{CHSO}_3\text{H})_n$ and $-(\text{CH}_2-\text{CHSO}_3^-\text{M}^+)_n$, wherein M is an alkali or alkaline earth metal and n has a value of from 5 to 100. In a second preferred

- 6 -

embodiment, R' and R'' are alkylene carboxylates of the general form $-R_3\text{-COOH}$ and $-R_3\text{-COO}^-\text{M}^+$, wherein R₃ is a C₁ to C₄ alkylene group, C₁ being especially preferred, and M is an alkali or alkaline earth metal.

5

The hydrophobic vinyl polymer can be attached to the polysaccharide backbone through the hydroxyl group or through any of the carbon atoms on the sugar. The polymer chains can be present at irregular intervals on the 10 polysaccharide chain and it is not critical that they be present at regular intervals. Up to 50% homopolymer may be present without impairing soil release performance. The anionic group is attached to the polysaccharide backbone through the hydroxyl group, either primary or secondary. It 15 is not essential that anionic substituents be present on each of the sugar rings.

It is not essential to remove any unreacted polysaccharide that may be present in the final product obtained by graft 20 copolymerisation and anionic modification of the polysaccharide.

The polysaccharide, which is the hydrophilic part of the molecule, is preferably chosen from cellulose, guar gum, 25 starch and tamarind kernel powder but is not limited by the same. More preferably the polysaccharide is starch. The starch can be any native starch and includes those derived from wheat, rice, oat, tapioca, maize, potato, sorghum, arrowroot or their mixtures thereof. Alternatively, acid or 30 enzymatically degraded starch or oxidised starch or their

- 7 -

mixtures or their mixtures thereof with the native starches can also be used.

When starch is the preferred polysaccharide, it may be in the 5 native form or gelatinised form. The term gelatinisation refers to rupture of the starch granule at elevated temperatures in presence of water.

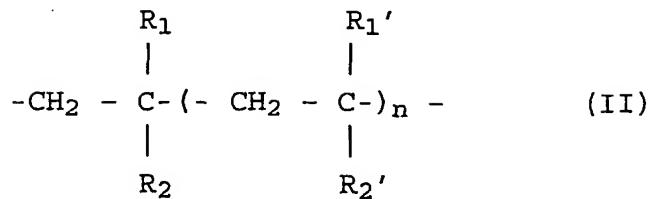
The hydrophobic modification is provided by a hydrophobic 10 vinyl polymer (R in Formula I) grafted onto the polysaccharide backbone. The polymers of vinyl monomers like acrylic monomers, vinyl acetate, styrene and substituted styrenes are especially preferred. The molecular weight of each of the hydrophobic vinyl polymer chains is preferably 15 500-5,000,000, more preferably from 2000-500,000 and most preferably from 5000-100,000.

The amount of the hydrophobic vinyl polymer is preferably 0.1-10% by weight of the polysaccharide, more preferably from 20 1-5% by weight of the polysaccharide.

Preferably, acrylic monomers are used for graft 25 copolymerisation. The hydrophobic acrylic polymers especially suitable for the present invention are shown below having the general formula II:

- 8 -

5



wherein R_1 and R'_1 may or may not be the same and represent
 $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$.

10

and wherein R_2 and R'_2 may or may not be the same and
represent $-\text{COOCH}_3$, $-\text{COOC}_2\text{H}_5$, $-\text{COOC}_3\text{H}_7$.

15 Particularly preferred is poly (methyl acrylate) wherein R_1
 $= \text{R}'_1 = \text{H}$ and $\text{R}_2 = \text{R}'_2 = -\text{COOCH}_3$.

20 The anionic group, which may be a group which possesses a
carboxylic or a sulphonic acid head group or a salt thereof,
is distributed along the backbone of the polysaccharide. The
compounds of the invention may contain both groups with
carboxylic acid or sulphonic acid head groups (or their
salts) as anionic substituents.

25 The amount of the anionic substituent is preferably 0.1-10%
by weight of the polysaccharide, more preferably from 0.1-5%
by weight of the polysaccharide.

30 Preferred examples of anionic reagents for effecting anionic
modification of the polysaccharide are halocarboxylic acids
or their salts and vinyl sulphonic acid or their salts or

- 9 -

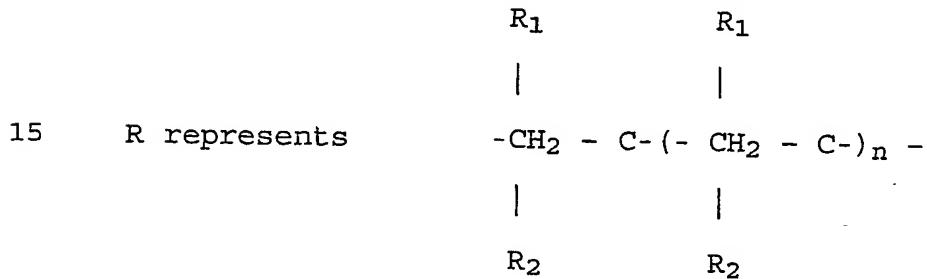
their mixtures thereof. More preferably the halocarboxylic acids are used as anionic reagents. Chloroacetic acid is especially preferred.

5 Examples of preferred modified polysaccharides

The following formulae are representative examples of anionic, hydrophobic polysaccharides of the invention (formula I).

10

In the figures,



$R_1 = H$ and $R_2 = -COOCH_3$

20

and $R' = -CH_2COOH$.

- 10 -

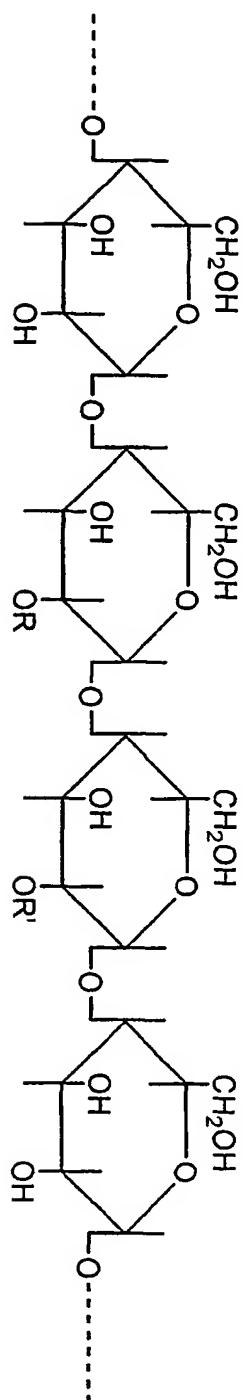
5

10

15

20

25



FORMULA III

30

FIG 1: ANIONIC HYDROPHOBIC GRAFT COPOLYMER OF STARCH

- 11 -

5

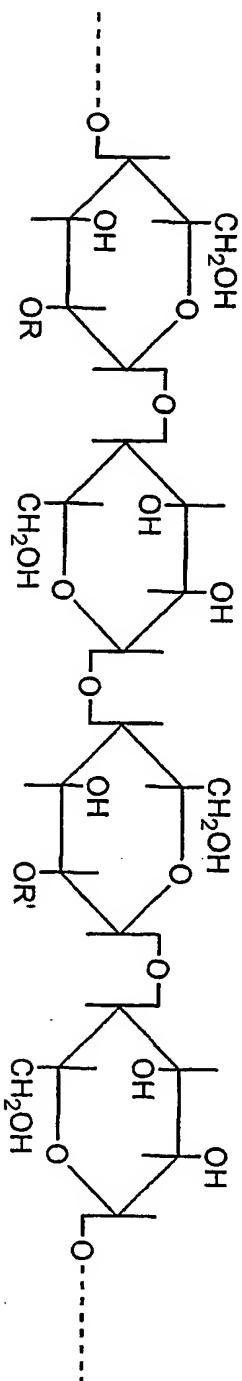
10

15

20

25

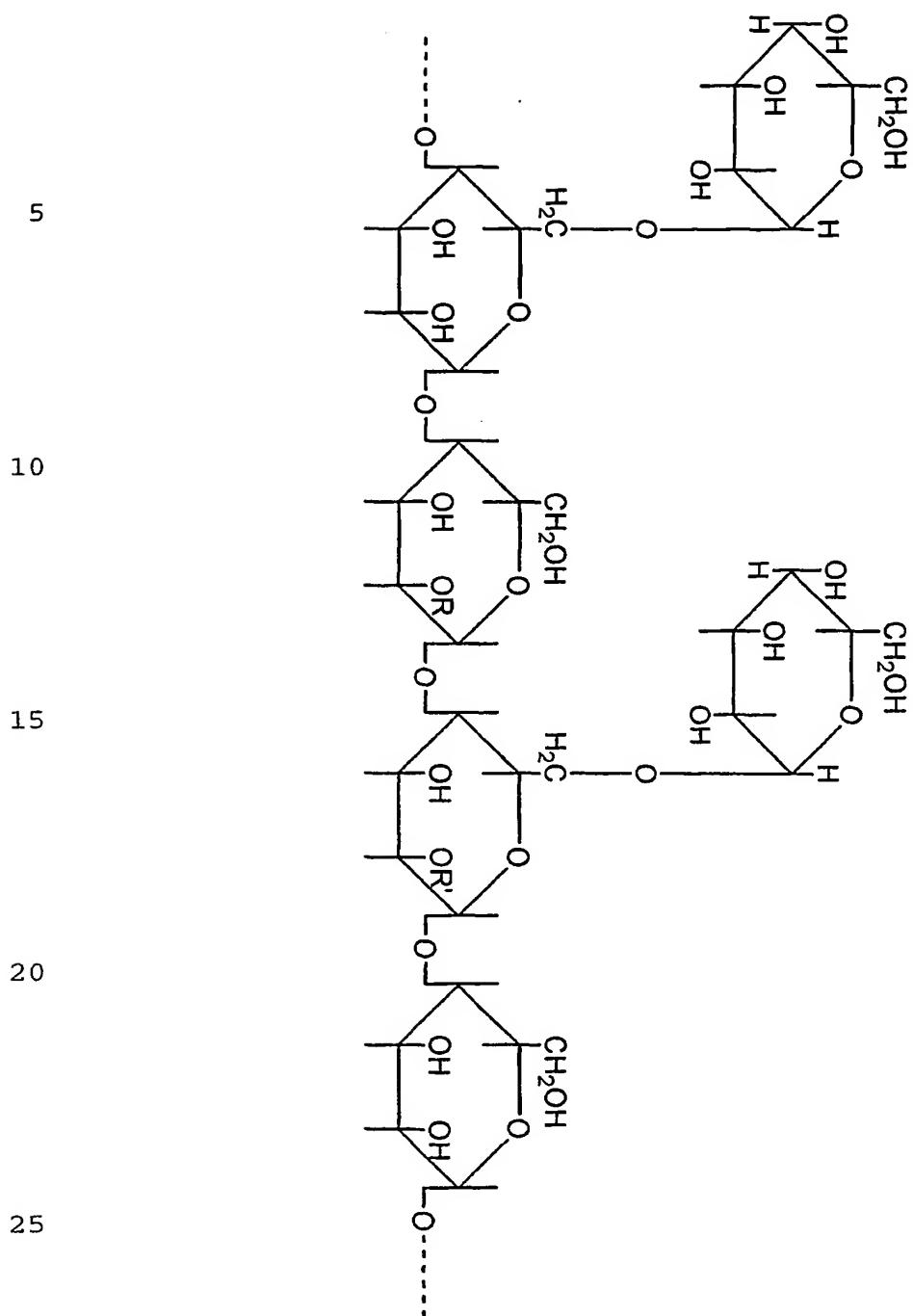
30



FORMULA IV

FIG 2: ANIONIC HYDROPHOBIC GRAFT COPOLYMER OF CELLULOSE

- 12 -



FORMULA V

30

FIG 3: ANIONIC HYDROPHOBIC GRAFT COPOLYMER OF GUAR GUM

- 13 -

5

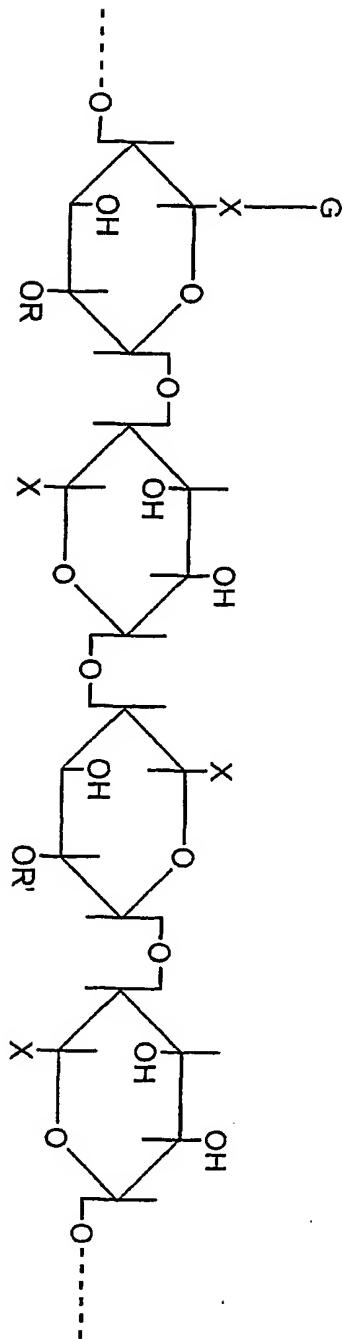
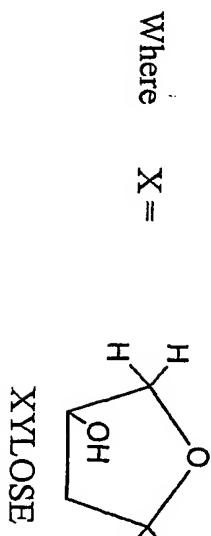
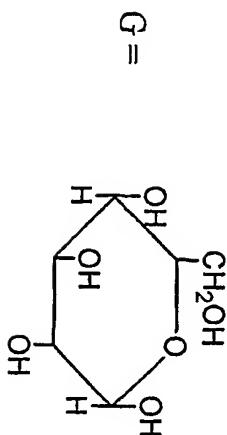
10

15

20

25

GALACTOSE



FORMULA VI

30 FIG 4: ANIONIC HYDROPHOBIC GRAFT COPOLYMER OF TAMARIND GUM

- 14 -

Preparation of the anionic, hydrophobic polysaccharides

The soil release polymers of the invention are prepared by
a) graft copolymerisation and b) anionic modification of the
5 polysaccharide. It is not particularly relevant for the
present invention as to which step is carried out first.
Preferably, the step of graft copolymerisation of the
polysaccharide is carried out first, followed by anionic
modification.

10

Both graft copolymerisation and anionic modification of the
polysaccharide can take place through the primary and/or the
secondary hydroxyl groups on the polysaccharide backbone.
Graft copolymerisation can also be initiated by H abstraction
15 from the monosaccharide residue.

Graft copolymerisation is carried out by contacting the redox
initiator, such as ferrous ammonium sulphate and hydrogen
peroxide or ceric ammonium nitrate and dilute nitric acid,
20 with the polysaccharide in an aqueous medium. A preferred
temperature range is 20-60°C., more preferably from 30-40°C.
It is preferable to add an entrainer, an example of which is
urea. When the ferrous ammonium sulphate and hydrogen
peroxide system is used as the redox initiation, it is
25 preferable to also add ascorbic acid. The hydrophobic
monomer is added and subsequent polymerisation takes place to
yield the polymer of the invention.

The hydrophobic graft copolymer so prepared is preferably
30 reacted with a carboxylating or sulphonating reagent
selected from halocarboxylic acid, an alkali or alkaline

- 15 -

earth metal salt of a halocarboxylic acid, vinyl sulphonic acid or the alkali or alkaline earth metal salt of the vinyl sulphonic acid. It is preferable to use haloacetic acid, more preferably chloroacetic acid, to provide anionic groups on the polysaccharide. The process of anionic modification 5 may be carried out in presence of a solvent such as water/isopropanol mixtures or as a dry process.

When the soil release polymer of the invention is prepared 10 from native starch, it is preferred to subject the same to a temperature of 70-90°C in presence of water, to make the soil release polymer water soluble.

Fabric treatment and detergent compositions

15 The soil release polymer of the invention may be used to treat fabric by incorporating it into detergent compositions, rinse conditioners or other fabric treatment compositions. It can also be used simply as an aqueous 20 solution which can be applied to the fabric to enhance soil removal from the fabric.

The polymers of the invention are suitably incorporated at the level of 0.01-10 wt%, preferably 0.5-5 wt%, of the 25 detergent or fabric treatment composition.

The soil release polymers may advantageously be incorporated into built laundry detergent compositions suitable for heavy duty use. A preferred detergent composition in accordance 30 with the invention may contain from 5 to 40 wt% of detergentsurfactant (detergent-active material), from 5 to 80 wt% of

- 16 -

detergency builder, and from 0.01 to 10 wt%, preferably from 0.5 to 5 wt%, of the soil release polymer of the invention.

Apart from the polymers of the invention, the detergent 5 formulations also contain as in conventional formulations, detergent actives (surfactants) and builders and auxiliaries. Auxiliaries include sequestrants, dye-transfer inhibitors, perfumes, bleaches, enzymes, floourescers, optical brighteners, fungicides, germicides, hydrotropes etc.

10

The detergent composition may be in any physical form, for example, powder, tablet, bar, paste or liquid.

15 The detergent active material is generally chosen from anionic, nonionic, cationic, zwitterionic detergent active compounds and mixtures thereof.

Anionic surfactants which can be used in the compositions of the invention are both soap and non-soap detergents 20 compounds. Especially suitable anionic detergent active compounds are water soluble salts of organic sulphuric reaction products having in the molecular structure an alkyl radical containing from 8 to 22 carbon atoms, and a radical chosen from sulphonic acid or sulphur acid ester radicals 25 and mixtures thereof.

The preferred water-soluble synthetic anionic detergent active compounds are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and 30 magnesium) salts of higher alkyl benzene sulphonates and mixtures with olefin sulphonates and higher alkyl sulphates, .

- 17 -

and the higher fatty acid monoglyceride sulphates. The most preferred anionic detergent active compounds are higher alkyl aromatic sulphonates such as higher alkyl benzene sulphonates containing from 6 to 20 carbon atoms in the 5 alkyl group in a straight or branched chain, particular examples of which are sodium salts of higher alkyl benzene sulphonates or of higher-alkyl toluene, xylene or phenol sulphonates, alkyl naphthalene sulphonates, ammonium diethyl naphthalene sulphonate, and sodium dinonyl naphthalene 10 sulphonate.

Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with 15 an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of 20 balance between hydrophilic and hydrophobic elements.

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with 25 ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates 30 of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensate containing from 40

to 80% of polyoxyethylene radicals by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides of structure R_3NO , where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each 5 methyl, ethyl or hydroxyethyl groups, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure R_3PO , where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance 10 dimethyldodecylphosphine oxide; and dialkyl sulphoxides of structure R_2SO where the group R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid 15 alkylolamides and alkyl mercaptans.

Suitable amphoteric detergent-active compounds that 20 optionally can be employed are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 carbon atoms and an aliphatic radical substituted by an anionic water-solubilizing group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane sulphonate and sodium N-2-hydroxydodecyl-N-methyltaurate. Suitable cationic detergent-active compounds are quaternary 25 ammonium salts having an aliphatic radical of from 8 to 18 carbon atoms, for instance cetyltrimethyl ammonium bromide.

Suitable zwitterionic detergent-active compounds that 30 optionally can be employed are derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds

- 19 -

having an aliphatic radical of from 8 to 18 carbon atoms and an aliphatic radical substituted by an anionic water-solubilising group, for instance 3-(N-N-dimethyl-N-hexadecylammonium), propane-1-sulphonate betaine, 3-

5 (dodecylmethyl sulphonium) propane-1-sulphonate betaine and 3-(cetyl methylphosphonium) ethane sulphonate betaine.

Further examples of suitable detergent-active compounds are compounds commonly used as surface-active agents given in

10 the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

The detergency builders used in the formulation are

15 preferably inorganic and suitable builders include alkali metal aluminosilicates (zeolites), alkali metal carbonate, sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), citrates, sodium nitrilotriacetate (NTA) and combinations of these. Builders may suitably be used in 20 amounts ranging from 5 to 80 wt%, preferably from 10 to 60 wt%.

The detergent compositions of the invention may also contain any other suitable ingredients. These may be selected from,

25 but are not limited to, bleaches, bleach precursors, bleach stabilisers (heavy metal sequestrants), photobleaches, enzymes, other polymers, foam boosters, foam controllers, fluorescers, fillers, flow aids, fabric conditioning agents, perfumes, colourants, and coloured speckles.

- 20 -

The polymers of the invention may also be used as part of a fabric washing kit, as part of a sachet or can be microencapsulated.

- 5 A fabric washing kit may comprise two enclosures separated from each other. It is preferred that one enclosure is big and the other small. The big enclosure contains the detergent formulation and the small enclosure the polymer. An instruction sheet contains directions for the use of the
- 10 two components including the proportions and conditions under which these are to be used. The kit may also contain a dispensing means to aid the washing using the two components in the desired proportions.
- 15 A preferred kit according to the invention is a plastic container having two separate chambers. A first bigger chamber holds the detergent composition. The second small chamber has a volume capacity not greater than about 10% of the big chamber and holds the soil release polymer of the
- 20 invention.

The polymer/detergent composition may also be packaged in single dose sachet having a compartment in which the two components are housed in a manner such that they come into contact when the contents are discharged from the sachet. It is also possible to microencapsulate the polymer and provide the product in a premixed form. Other forms of packagings are also included within the scope of invention.

- 21 -

The invention is illustrated further by the following non-limiting examples, in which parts and percentages are by weight unless otherwise stated.

5 EXAMPLES

Example 1

Synthesis of Soil Release Polymer

10

100 g urea was dissolved in 1 litre of distilled water in a flask equipped with a stirrer and a thermometer. 1 kg of tapioca starch, 1 g ferrous ammonium sulphate and 5 g ascorbic acid, 50 ml methyl acrylate were added sequentially and the mixture was stirred. 10 ml hydrogen peroxide (30% w/v) was then added, the reaction mixture stirred and then filtered. The reaction was conducted at 30°C. The starch-graft-poly (methyl acrylate) obtained was repeatedly washed with water and then dried at 100°C.

20

250 g of chloroacetic acid and 240 g of sodium hydroxide was dissolved in water and mixed under stirring maintaining a temperature of <20°C. 40 g urea was then added to the mixture. 1 kg of the above starch-graft-poly (methyl acrylate) was taken in a mixer and the chloroacetic acid-sodium hydroxide mixture was then sprayed on to the same under stirring. The mixture was left for 24 hours at 60°C and then dried to 11% moisture.

30

Example 2Demonstration of soil removal properties of the polymer

5 A standard detergent formulation without a soil release polymer was formulated (Comparative Example A). A detergent formulation incorporating the polymer of Example 1 was also prepared. The formulation details are presented in Table 1.

10 Table 1

| Composition % wt. | Comparative Example A | Example 1 |
|---------------------------------|-----------------------|-----------|
| Linear alkyl benzene sulphonate | 20 | 20 |
| Sodium tripolyphosphate | 27 | 27 |
| Soda | 15 | 15 |
| Alkaline silicate | 10 | 10 |
| Fillers | 15 | 15 |
| Soil Release Polymer | - | 2 |
| Water | To 100 | To 100 |

Soil release is determined by improvement in detergency.

15 100% cotton and 100% polyester fabric were used in the study. The fabric was cut into swatches of dimension 5" X 5". The swatches were soiled using a) oily soil and b) particulate soil (carbon soot). The oily soil could be sebum prepared in the lab or motor oil. A red dye at a

- 23 -

concentration of 0.025% is added to the oil to clearly determine oil removal from the fabric.

Commercially available fabrics presoiled with a mixture of 5 oily and particulate soil (WFK 30D was pre-soiled polyester and WFK 10D was pre-soiled cotton) were also used.

0.2g of soil along with oil red dye at a concentration of 0.025% was loaded on to each of the test swatches and the 10 stain was allowed to wick for a period of 24 hrs. Initial reflectance measurement at 520 nm was taken, on a Milton Roy Color Scan II. 520 nm is the wavelength at which the red dye absorbs, hence it is used to monitor soil removal.

15 For particulate soil loading, carbon soot was deposited to the cloth piece to get a reflectance of 55. The reflectance was determined at 460 nm.

20 The fabrics mentioned above were washed using the detergent compositions of Comparative Example A and Example 1, maintaining 10 replicates for each. Detergent solutions of concentration 5g/l were then prepared.

25 Test swatches were washed in a tergotometer in the detergent solution for a period of 15 minutes. Reflectance measurements were taken at 520nm (for oily soil) or 460 nm (for particulate soil and WFK 10D and 30D). The difference in reflectance of the soiled fabrics before and after washing was noted and represented as $\Delta R520^*$ or $\Delta R460^*$.

- 24 -

The improvement in soil removal for oily soil was determined as follows:

Improvement in oily soil removal ($\Delta\Delta R520^*$) = $\Delta R520^*$ (for

5 Example 1) - $\Delta R520^*$ (for Comparative Example A).

The improvement in soil removal for particulate and mixtures of oily and particulate was determined as follows:

10 Improvement in soil removal ($\Delta\Delta R460^*$) = $\Delta R460^*$ (for Example 1)
 - $\Delta R460^*$ (for Comparative Example A)

The results of the tergotometer washes following the above detergency test procedure for removal of soils from polyester
 15 are presented in Table 2. Test results for cotton are presented in Table 3.

Table 2 - Polyester

| | | |
|--------------------------------------|-----------------------|-----|
| Particulate soil | $\Delta\Delta R460^*$ | 2.4 |
| Artificial sebum | $\Delta\Delta R520^*$ | 1.6 |
| Motor oil | $\Delta\Delta R520^*$ | 2.5 |
| Mixture of oily and particulate soil | $\Delta\Delta R460^*$ | 2.0 |

20

Table 3 - Cotton

| | | |
|--------------------------------------|-----------------------|-----|
| Particulate soil | $\Delta\Delta R460^*$ | 3.0 |
| Artificial sebum | $\Delta\Delta R520^*$ | 0.5 |
| Motor oil | $\Delta\Delta R520^*$ | 0.5 |
| Mixture of oily and particulate soil | $\Delta\Delta R460^*$ | 2.0 |

- 25 -

The above reflectance measurements indicate benefits in use of an anionic, hydrophobic graft copolymer of starch in removal of both oily and particulate soil or their mixture on both polyester and cotton fabric.

5

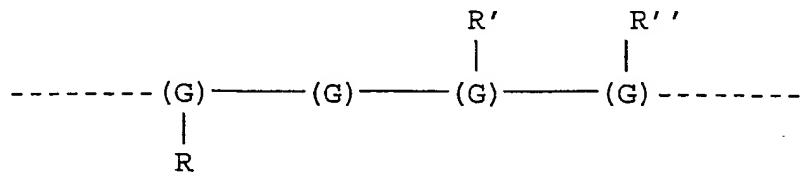
CLAIMS

1. Anionic, hydrophobic polysaccharide characterised in
5 that it is a graft copolymer of a polysaccharide having
anionic substituents with an ethylenically unsaturated
monomer, the copolymer having a polysaccharide backbone
carrying grafted hydrophobic vinyl polymeric groups
derived from the ethylenically unsaturated monomer, and
10 anionic substituents.

2. Anionic, hydrophobic polysaccharide according to
claim 1, characterised in that the anionic substituents
15 are selected from groups which possess a carboxylate or
a sulphonate head group.

3. Anionic, hydrophobic polysaccharide characterised by
the general formula I:

20



30

wherein R is a hydrophobic vinyl polymer, R' and R'',
which may or may not be the same, represent a group
which possesses a carboxylic acid or a sulphonic acid
head group or salts thereof and G is a monosaccharide
or substituted monosaccharide.

- 27 -

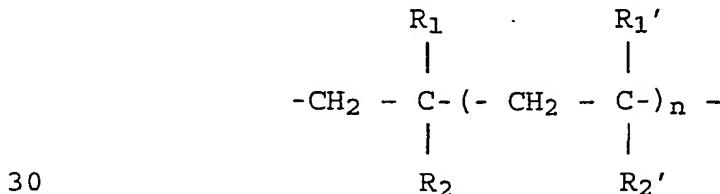
4. Anionic, hydrophobic polysaccharide according to
claim 3, characterised in that R_{1'} and R'', which may
or may not be the same, are polymeric vinyl sulphonates
selected from -(CH₂-CHSO₃H)_n and -(CH₂-CHSO₃⁻M⁺)_n,
5 wherein M is an alkali or alkaline earth metal and n
has a value of from 5 to 100.
5. Anionic, hydrophobic polysaccharide according to
claim 3, characterised in that R' and R'', which may or
10 may not be the same, are selected from -R₃-COOH and
-R₃-COO⁻M⁺, wherein R₃ is a C₁ to C₄ alkylene group and
M is an alkali or alkaline earth metal.
6. Anionic, hydrophobic polysaccharide according to
claim 5, characterised in that R' = R'' = -CH₂-COOH or
15 its metal salt.
7. Anionic, hydrophobic polysaccharide according to any
preceding claim, characterised in that the amount of
20 the hydrophobic vinyl polymer is 0.1-10% by weight of
the polysaccharide.
8. Anionic, hydrophobic polysaccharides according to
claim 7, characterised in that the amount of the
25 hydrophobic vinyl polymer is 1-5% by weight of the
polysaccharide.
9. Anionic, hydrophobic polysaccharide according to any
preceding claim, characterised in that the amount of

- 28 -

anionic substituent is 0.1-10% by weight of the polysaccharide.

10. 10. Anionic, hydrophobic polysaccharide according to
5 claim 9, characterised in that the amount of anionic
substituent is 0.1-5% by weight of the polysaccharide.
11. 11. Anionic, hydrophobic polysaccharide according to any
preceding claim, characterised in that the hydrophobic
10 vinyl polymer has a molecular weight from 500 to
5,000,000.
12. 12. Anionic, hydrophobic polysaccharide according to
claim 11, characterised in that the hydrophobic vinyl
15 polymer has a molecular weight from 2000 to 500,000.
13. 13. Anionic, hydrophobic polysaccharide according to
claim 12, characterised in that the hydrophobic vinyl
polymer has a molecular weight from 5000 to 100,000.
- 20 14. 14. Anionic, hydrophobic polysaccharide according to any
one of claims 3 to 13, characterised in that R is an
acrylic polymer, having the general formula II

25



- 29 -

wherein R_1 and R_1' may or may not be the same and represent $-H$, $-CH_3$, $-C_2H_5$, and wherein R_2 and R_2' may or may not be the same and represent $-COOCH_3$, $-COOC_2H_5$, $-COOC_3H_7$.

5

15. Anionic, hydrophobic polysaccharide according to claim 14, characterised in that $R_1 = R_1' = H$ and $R_2 = R_2' = -COOCH_3$.
- 10 16. Anionic, hydrophobic polysaccharide according to any preceding claim, characterised in that the polysaccharide is selected from starch, modified starches, cellulose, guar gum, and tamarind gum.
- 15 17. Anionic, hydrophobic polysaccharide according to claim 16, characterised in that the polysaccharide is starch.
18. A process for the preparation of an anionic, hydrophobic polysaccharide according to any one of claims 1 to 17, characterised in that it comprises graft copolymerisation and anionic modification of a polysaccharide.
- 20 25 19. A process according to claim 18, characterised in that it comprises graft copolymerisation of the polysaccharide or the anionically modified polysaccharide using a redox initiator.

- 30 -

20. A process according to claim 19, characterised in that it comprises graft copolymerisation of the polysaccharide or the anionically modified polysaccharide using ferrous ammonium sulphate and 5 hydrogen peroxide as the redox initiator.
21. A process according to any one of claims 18 to 20, characterised in that it comprises anionic modification of the polysaccharide or the graft copolymerised 10 polysaccharide using halocarboxylic acid or its salt or mixtures thereof.
22. A process according to claim 21, characterised in that the halocarboxylic acid is chloroacetic acid. 15
23. A process according to any one of claims 18 to 20, characterised in that it comprises anionic modification of the polysaccharide or the graft copolymerised polysaccharide using a vinyl sulphonate acid or its salt 20 or mixtures thereof.
24. A fabric treatment composition comprising a fabric treatment agent, characterised in that it further comprises from 0.01 to 10 wt% of an anionic, 25 hydrophobic polysaccharide according to any one of claims 1 to 17.
25. A detergent composition comprising from 5 to 60 wt% of a detergentsurfactant, characterised in that it further comprises from 0.01 to 10 wt% of an anionic, 30

- 31 -

hydrophobic polysaccharide according to any one of claims 1 to 17.

26. A detergent composition according to claim 25,
5 characterised in that it is a built laundry detergent composition comprising from 5 to 40 wt% of detergative surfactant, and from 5 to 80 wt% of detergency builder.
27. A detergent compositions according to claim 25 or
10 claim 26, characterised in that it comprises from 0.5 to 5 wt% of the anionic, hydrophobic polysaccharide according to any one of claims 1 to 17.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/EP 01/04942A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/22 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-------------------------|
| X | US 5 223 171 A (TOURNILHAC FLORENCE ET AL) 29 June 1993 (1993-06-29) claims 1-4; example 8 | 1-5, 11-16, 18, 24-27 |
| X | DE 43 16 746 A (HUELS CHEMISCHE WERKE AG) 24 November 1994 (1994-11-24) page 2, line 37 -page 3, line 20; claims | 1-4, 16, 18, 25 |
| A | GB 2 322 137 A (UNILEVER PLC) 19 August 1998 (1998-08-19) cited in the application claims; examples | 1, 3, 5-9, 11-20, 24-27 |
| A | US 5 227 446 A (HARTMANN HEINRICH ET AL) 13 July 1993 (1993-07-13) cited in the application claims | 1, 3, 5-9, 11-20 |
| | | -/- |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

24 October 2001

Date of mailing of the international search report

31/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gritter, A

INTERNATIONAL SEARCH REPORT

| | |
|-----------------|------------------|
| Intc | I Application No |
| PCT/EP 01/04942 | |

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US 4 925 588 A (BERROD GERARD ET AL) 15 May 1990 (1990-05-15) claims ----- | 1,2, 24-27 |
| A | US 3 558 499 A (GALVIN THOMAS J ET AL) 26 January 1971 (1971-01-26) column 2, line 67 -column 3, line 44; claims ----- | 1,16-18, 24-27 |

INTERNATIONAL SEARCH REPORT

nation on patent family members

Inte Application No
PCT/EP 01/04942

| Patent document cited in search report | | Publication date | | Patent family member(s) | | Publication date |
|--|---|------------------|----|-------------------------|------------|------------------|
| US 5223171 | A | 29-06-1993 | FR | 2663948 A1 | 03-01-1992 | |
| | | | AT | 111152 T | 15-09-1994 | |
| | | | CA | 2045921 A1 | 03-01-1992 | |
| | | | DE | 69103833 D1 | 13-10-1994 | |
| | | | DE | 69103833 T2 | 20-04-1995 | |
| | | | EP | 0465287 A1 | 08-01-1992 | |
| | | | IE | 912301 A1 | 15-01-1992 | |
| | | | JP | 4226599 A | 17-08-1992 | |
| | | | PT | 98172 A | 31-08-1993 | |
| DE 4316746 | A | 24-11-1994 | DE | 4316746 A1 | 24-11-1994 | |
| GB 2322137 | A | 19-08-1998 | | NONE | | |
| US 5227446 | A | 13-07-1993 | DE | 4003172 A1 | 08-08-1991 | |
| | | | AU | 628712 B2 | 17-09-1992 | |
| | | | AU | 7017291 A | 08-08-1991 | |
| | | | CA | 2034943 A1 | 04-08-1991 | |
| | | | DE | 59107176 D1 | 15-02-1996 | |
| | | | EP | 0441197 A2 | 14-08-1991 | |
| | | | ES | 2081377 T3 | 01-03-1996 | |
| | | | JP | 4356513 A | 10-12-1992 | |
| US 4925588 | A | 15-05-1990 | FR | 2609065 A1 | 01-07-1988 | |
| | | | FR | 2615526 A1 | 25-11-1988 | |
| | | | AT | 57713 T | 15-11-1990 | |
| | | | DE | 3765773 D1 | 29-11-1990 | |
| | | | DK | 684387 A | 25-06-1988 | |
| | | | EP | 0279134 A1 | 24-08-1988 | |
| | | | IE | 350687 L | 24-06-1988 | |
| | | | JP | 63219683 A | 13-09-1988 | |
| | | | PT | 86467 A ,B | 01-01-1988 | |
| | | | FI | 882372 A | 21-11-1988 | |
| | | | NO | 881261 A | 21-11-1988 | |
| US 3558499 | A | 26-01-1971 | | NONE | | |

BEST AVAILABLE COPY